

Ab initio molecular dynamics study of the desorption of D_2 from Si(100)

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Ab initio molecular dynamics calculations of deuterium desorbing from Si(100) have been performed in order to monitor the energy redistribution among the various D_2 and silicon degrees of freedom during the desorption process. The calculations show that a considerable part of the potential energy at the transition state to desorption is transferred to the silicon lattice. The deuterium molecules leave the surface vibrationally hot and rotationally cold, in agreement with thermal desorption experiments; the mean kinetic energy, however, is larger than found in a laser-induced desorption experiment. We discuss possible reasons for this discrepancy.

Hydrogen adsorption on and desorption from Si surfaces are of great technological relevance for, e.g., the etching and passivation of Si surfaces or the growth of Si crystals (see, e.g., Ref. [1] and references therein). Besides, the dynamics of the hydrogen interaction with Si surfaces is also of fundamental interest caused, among others, by the so-called barrier puzzle: While the sticking coefficient of molecular hydrogen on Si surfaces is very small [2,3,4,5] indicating a high barrier to adsorption, in desorption experiments an almost thermal mean kinetic energy of the molecules was found [6] indicating a low adsorption barrier. In order to explain this puzzle it was suggested to take the strong surface rearrangement of Si upon hydrogen adsorption into account [6]: The hydrogen molecules impinging on the Si substrate from the gas phase typically encounter a Si configuration which is unfavorable for dissociation, while desorbing hydrogen molecules leave the surface from a rearranged Si configuration with a low barrier. Unfortunately, at this point it is unclear how low the barrier really is, because the results for the dissociative adsorption probability of references [3] and [5] differ by almost three orders of magnitude. This difference translates into a difference of the minimum barrier heights measured in these two experiments of about 0.4 eV.

Total-energy calculations using the cluster approach [7,8,9,10] have found activation barriers for associative desorption of about 1 eV. With the assumption of a lattice rearrangement energy of about 0.7 eV the experimental adsorption results of Refs. [4,5] and the desorption results of Ref. [6] could be reproduced by quantum dynamical model calculations [11,12]. Still the exact adsorption and desorption mechanism is strongly debated in the system $H_2/Si(100)$. In view of density-functional theory (DFT) calculations for Si(100) a lattice-relaxation energy of 0.7 eV seemed to be too high [13]. Indeed, in detailed DFT calculations of the $H_2/Si(100)$ potential energy surface (PES) using the supercell approach [14,15,16] the adsorption barriers were found to be only 0.3 - 0.4 eV with a substrate rearrangement energy of about 0.15 eV.

Based on the slab calculations [14] and approximating the high-dimensional PES by a three-dimensional one,

two different quantum dynamical studies were performed [17,18], where the relaxation of the Si substrate upon hydrogen adsorption was represented by one idealized Si phonon coordinate. Although both calculations used the same *ab initio* energies as a source, the results of the dynamical calculations did not agree quantitatively. However, in both studies the dynamical coupling of the desorption path to the Si substrate was low.

In order to help clarifying these various confusing and in fact partially conflicting results we have studied the associative desorption of D_2 from Si(100) by determining how the potential energy at the barrier is distributed over the various degrees of freedom of this system (hydrogen vibration, rotation, and translational energy, and vibrations of the Si substrate). The calculation of PESs is an important prerequisite for understanding reaction dynamics. For a quantitative analysis, however, a calculation of the dynamics is indispensable. Since the substrate relaxation plays such an important role for the hydrogen desorption from Si(100), a proper description of the Si dynamics during the desorption event is required. We feel that a reliable dynamical calculation requires the consideration of the six degrees of freedom of the hydrogen molecule plus at least two degrees of freedom of the Si surface (dimer stretch and tilt). A *quantum* dynamical treatment of the desorption dynamics taking these eight degrees of freedom simultaneously into account is presently not possible. The record still stands at six dimensions [19]. We have therefore performed *ab initio* molecular dynamics calculations to monitor the energy distribution of D_2 molecules desorbing from Si(100). This allows us to assess the dynamical consequences of the calculated PES. We will show that the deuterium molecules leave the surface vibrationally hot and rotationally cold, in agreement with thermal desorption experiments [20]. Indeed, approximately 0.1 eV of the potential energy at the transition state is transferred to substrate vibrations. Still, also the molecules receive a noticeable kinetic energy which is at variance with a laser-induced desorption experiment [6]. We will discuss possible reasons for this interesting discrepancy.

In the *ab initio* molecular dynamics approach [21,22] the forces necessary to integrate the classical equations

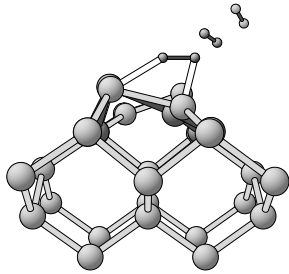


FIG. 1. Snapshots of a trajectory of D_2 desorbing from Si(100) starting at the transition state with the Si atoms initially at rest. The dark Si atoms correspond to the Si positions after the desorption event.

of motion are determined by DFT calculations. The exchange-correlation functional is treated in the generalized gradient approximation (GGA) [23]. For the hydrogen atoms the full $1/r$ potential is used. In previous slab studies the total energies were calculated within the local density approximation (LDA) with *a posteriori* GGA corrections [15]. The main effects of using the GGA in the complete self-consistent cycle are a small increase of the theoretical lattice constant of Si [24] and a slight rise in the barrier height from $E_b = 0.3$ eV [15] to $E_b = 0.4$ eV. To correctly represent the up and down buckling of the clean Si(100) surface we use a (2×2) surface unit cell. The Si slab consists of five atomic layers. The topmost three of them are free to move in the molecular dynamics simulations, while the remaining two layers are fixed at their bulk positions. The density-functional calculations are performed with two \mathbf{k} -points in the irreducible part of the Brillouin zone and 40 Ry cutoff energy. The equations of motion are numerically integrated within a predictor-corrector scheme with a time step of 1.2 fs.

Since the barrier to associative desorption of hydrogen from Si(100) is rather high ($E_d \approx 2.5$ eV [15,25,26]), there is no sense in performing molecular dynamics calculations starting with the deuterium atoms at the adsorption sites because of the extremely low number of desorption events. Therefore we started the desorption trajectories close to the transition state for dissociative adsorption which was determined in the earlier study [15]. The desorbing D_2 molecule originates from two D atoms which were bonded to the same Si dimer; this pre-pairing mechanism [16] is consistent with the observed first-order kinetics in experiment [25,26]. In total we have computed 42 trajectories of D_2 desorbing from Si(100). Eight trajectories were determined with the Si lattice initially at rest, i.e., at a surface temperature of $T_s = 0$ K. Figure 1 shows snapshots of such a calculated trajectory. The dark Si atoms correspond to the relaxation of the Si lattice after the desorption event. Approximately 0.1 eV of the potential energy at the transition state is trans-

ferred to vibrations of the Si lattice which is a rather large amount compared to what is known from other systems [27]. At the transition state the D-D distance is about 40% larger than the D_2 the gas-phase bond length; consequently molecular vibrations are excited during the desorption, as is well known for a long time in associative desorption studies (see, e.g., ref. [27]). Due to the strong anisotropy of the PES, molecular rotations are very effectively quenched during the desorption event.

The mean kinetic energy of D_2 desorbing from Si(100) was determined by laser induced thermal desorption at a rather high surface temperature of $T_s \approx 920$ K. In order to simulate these experimental conditions, we have performed *ab initio* molecular dynamics calculations with initial conditions corresponding to the experimental surface temperature. The system was allowed to equilibrate for more than 500 fs, whereby the deuterium atoms were kept close to the transition state by auxiliary forces F_i^c acting on the deuterium atoms

$$F_i^c(R_i) = \begin{cases} 0 & : |\Delta R_i| < \Delta R_i^0 \\ -k \operatorname{sign}(\Delta R_i) \cdot (|\Delta R_i| - \Delta R_i^0) & : |\Delta R_i| \geq \Delta R_i^0 \end{cases} \quad (1)$$

with

$$\Delta R_i = R_i - R_i^{tr}. \quad (2)$$

The force constant $k = 5.2 \times 10^2 \text{ Nm}^{-1}$ is taken from the vibrations of the free hydrogen molecule. The index i , $i = 1, 2, 3$, denotes the cartesian coordinates, R_i^{tr} are the transition state coordinates of the two D atoms (see Fig. 1). The extra-force-free region is given by

$$\Delta R_i^0 = \begin{cases} 0.1 \text{ \AA} & : i = 1, 2 \\ 0.08 \text{ \AA} & : i = 3 \end{cases}, \quad (3)$$

so that the deuterium atoms in z -direction were kept closer to the transition state than in x - and y -direction.

The additional potential was switched off when no extra forces were acting on the D atoms, and the energy distribution of the D_2 molecules desorbing from the thermal surface was monitored. Simultaneously trajectories were run with the additional potential switched on so that the changes in the trajectories of the Si substrate atoms due to the desorption event could be followed. This trajectory was then also used for the next desorption event.

It is true that thermal desorption usually does not correspond to a genuine equilibrium situation since it is commonly studied in vacuum. However, desorption events are in general not effected by the presence or absence of gas molecules in front of the surfaces. This makes it possible to treat thermal desorption as if it corresponds to a thermal equilibrium situation [28]. From that it follows that we can assume that the phase space density in every point in real-space is given by a Boltzmann distribution, in particular at the transition state. In addition,

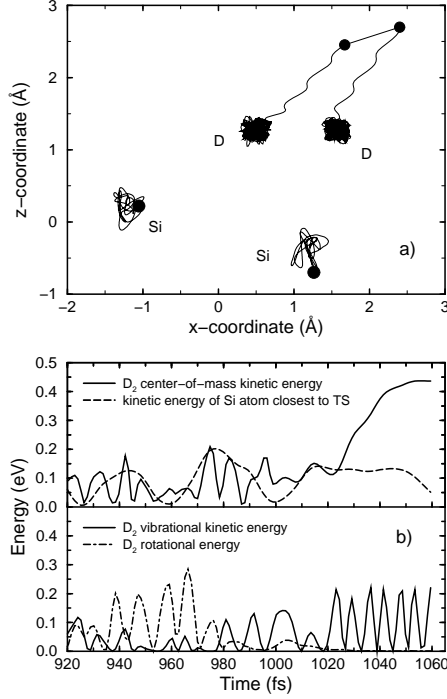


FIG. 2. Example of a thermal desorption trajectory which was run for 1060 fs. a) x and z coordinates of the trajectories of the two deuterium atoms and the two Si atoms of the dimer underneath the transition state (TS). The final positions of the atoms are marked by the large dots. b) energy redistribution as a function of the last 140 fs of the run-time of the trajectory. Upper panel, solid line: D_2 center-of-mass kinetic energy, dashed line: kinetic energy of the Si atom closest to the transition state (TS); lower panel, solid line: D_2 vibrational kinetic energy, dash-dotted line: D_2 rotational energy.

recrossings of trajectories at the transition state are very unlikely to occur in the system $D_2/Si(100)$. Due to the high binding energy there are large dissipative effects for adsorbing molecules; and for desorbing molecules there are no restoring forces in the gas phase. This allows the application of transition state theory [29] and equivalently also the assumption of thermal equilibrium for the initial desorption conditions at the transition state.

In total 34 “thermal” desorption trajectories were calculated. Figure 2 shows an example of such a trajectory with a total run-time of 1060 fs. For the first 1020 fs the molecular dynamics was run with the additional potential V^c . At $t = 1020$ fs the extra potential was switched off and the molecule was allowed to desorb. The projection of the trajectories of the desorbing deuterium molecule and of the Si dimer closest to the transition state onto the xz -plane is shown in Fig. 2a). Clearly the vibrational excitation of the desorbing D_2 molecule can be seen. In Fig. 2b) the energy redistribution during the last 140 fs

| | | | |
|---------------------------|--------------------|---------------------------|--------------------|
| $\langle E_{tot} \rangle$ | 0.72 ± 0.17 eV | $\langle E_{vib} \rangle$ | 0.11 ± 0.09 eV |
| $\langle E_{kin} \rangle$ | 0.58 ± 0.13 eV | $\langle E_{rot} \rangle$ | 0.03 ± 0.05 eV |

TABLE I. Mean energy distribution averaged over 34 trajectories of D_2 molecules desorbing from a $Si(100)$ surface at a surface temperature of $T_s = 920$ K ($k_B T_s = 0.079$ eV).

of the run is plotted. Besides the vibrational excitation the quenching of the rotational motion can be followed. Also the acceleration of the D_2 center-of-mass is obvious.

The mean total, kinetic, vibrational, and rotational energies of the D_2 molecules averaged over the 34 thermal desorption events are listed in table I (note that $k_B T_s = 0.079$ eV at $T_s = 920$ K.). The results show vibrational heating, i.e. $\langle E_{vib} \rangle > k_B T_s$, and rotational cooling, i.e. $\langle E_{rot} \rangle < k_B T_s$, in agreement with the experiment [20]. The D_2 center-of-mass kinetic energy, however, is much larger than the experimental value of $\langle E_{kin} \rangle^{exp} = 0.165$ eV $\gtrsim 2k_B T_s$ [6]. The difference between the experimental and theoretical results corresponds roughly to the barrier height $E_b = 0.4$ eV. A closer analysis of the trajectories reveals that still approximately 0.1 eV of the potential energy at the transition state is transferred to the Si lattice, but due to the Si lattice vibrations the mean adsorption barrier is increased by roughly the same amount. Possible contributions to the discrepancy between theory and experiment could be:

(i) *insufficient statistics* – Certainly 34 thermal trajectories are not enough in order to claim that a true thermal average has been performed. However, the widths of our distributions seem to be converged quite well and we are convinced that by sampling more points of the phase space at the transition state as initial conditions the excess translational energy of 0.4 eV would not disappear.

(ii) *quantum mechanical effects* – There are two important quantum mechanical effects not taken into account by classical molecular dynamics: tunneling and zero-point effects. Low-dimensional quantum dynamical studies of $D_2/Si(100)$ have already shown that tunneling is strongly suppressed due to the thickness of the barrier [17,18]. As for zero-point effects, it has been shown [14] that the sum of all zero-point energies of the hydrogen molecule at the transition state approximately equals the zero-point energy of hydrogen in the gas-phase. In such a situation zero-point effects cancel out as far as the center-of-mass kinetic energy is concerned since they lead to an almost constant energetic shift of the minimum energy paths in the hydrogen coordinates [30]. Hence we infer that quantum mechanical effects do not significantly change the kinetic energy of desorbing molecules.

(iii) *dissipation channels not considered* – A further channel for energy dissipation at surfaces is the excitation of electron-hole pairs. This channel is not taken into

account in the *ab initio* molecular dynamics simulations where the electrons are assumed to follow the ionic motion adiabatically in the electronic ground state. While electronic excitations of the H_2 molecule require a too large energy, the excitation of a surface exciton with a hole in the dangling bond at the upper Si atom and an electron in the lower Si dangling bond is in fact a possibility. This exciton might have some resemblance to that at the (110) surface of GasAs [31]. The described surface exciton at Si(100) will strongly couple to the lattice and bring the Si dimer in a geometry parallel to the surface. Thus, the H_2 desorption ends with an electronic state and geometry 0.2 eV higher than the ground state, and this energy would be taken out of the H_2 kinetic energy.

(iv) *limitations of the GGA functional* – It was recently shown that the GGA-PW91 functional used in our study underestimates the H_2 elimination barriers from silanes, i.e., small molecules [32]. On the other hand, energies for surface systems calculated from cluster models are sometimes seriously in error (see, e.g., Ref. [33]) and typically converge very slowly with cluster size. Hence results for small molecules are not directly transferable to surface systems. Still the validity of the GGA-PW91 functional for the barrier heights of H_2 /Si(100) certainly remains an open question since the application of GGA functionals for dissociation at surfaces is still a rather new field.

(v) *experimental uncertainties* – The desorption experiments were done with a Si sample with a high dopant concentration of $n \approx 10^{19} \text{ cm}^{-3}$. Therefore the Si(100) surface used in the experiment might have been metallic. It is well possible that for such a system the geometry of the clean surface is different from that of an undoped substrate. Thus, the final state of the desorption is changed and possibly also the geometry and energy of the transition state. In fact, also in Ref. [5] it had been speculated that high doping might influence the barrier heights in order to explain that the sticking probability for hydrogen molecules at Si(100) is much higher for a highly doped sample [3] than for a weakly doped system [5].

In addition, recent *ab initio* calculations indicate that laser melting of bulk silicon leads to a transition to a metallic liquid state [34] which could also occur during the laser-induced desorption used in the experiment. This would also change the geometrical and electronic structure at the transition state. Furthermore, at a metallic surface the excitation of electron-hole pairs might affect the desorption dynamics and, for example, enhance the probability of the above noted exciton state.

In conclusion, we have presented an *ab initio* molecular dynamics study of the desorption of D_2 from Si(100). The calculations give a qualified description of the desorption of hydrogen from undoped and good quality Si(100). While the energy distribution of the desorbing molecules in the vibrational and rotational degrees of freedom is in agreement with experiment [20], the excess translational energy is too large compared to the exper-

iment of Ref. [3]. This discrepancy might be caused by uncertainties in the determination of the interaction potential; however, it could also be due to the high doping of the Si sample used in the experiment of Ref. [3].

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